Ionic Liquid Crystals

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Superfluorinated Ionic Liquid Crystals Based on Supramolecular, Halogen-Bonded Anions

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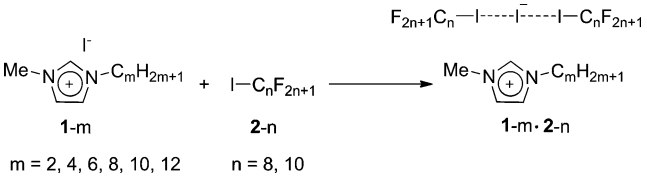
Abstract: *Unconventional ionic liquid crystals in which the liquid crystallinity is enabled by halogen-bonded supramolecular anions $[C_nF_{2n+1}\text{-}I\cdots I\cdots I\text{-}C_nF_{2n+1}]^-$ are reported. The material system is unique in many ways, demonstrating for the first time 1) ionic, halogen-bonded liquid crystals, and 2) imidazolium-based ionic liquid crystals in which the occurrence of liquid crystallinity is not driven by the alkyl chains of the cation.*

Ionic liquids are often defined as salts with melting points below 100 °C. Ionic liquids have several unique characteristics, such as high ionic conductivity, low volatility, and a lack of flammability, on account of which they are investigated extensively as new materials for electrochemical devices and as green solvents for materials synthesis and characterization.[1–5]

The properties of imidazolium-based ionic liquids are highly sensitive to the nature of the counteranion and can be tailored further through chemical modification of the organic cation. In particular, upon substituting the cation with long alkyl chain(s), some ionic liquids may exhibit liquid-crystalline properties, combining the attractive features of liquid crystals and ionic liquids.[6–9] The anisotropic conductivity of ionic liquid crystals, hereinafter referred to as ILCs, is of particular interest as it can find application in molecular electronics[10,11] or in dye-sensitized solar cells.[12–14]

In order to realize the potential of ILCs, there is high demand for novel types of ionic mesogens with tailored physical and/or chemical properties. Herein, we present a strategy for obtaining a new type of ILCs, in which the liquid crystallinity is enabled by the formation of supramolecular, halogen-bonded trimeric anions containing 1-iodoperfluoroalkane units, which encode calamitic mesomorphism. The supramolecular, halogen-bonded C–I···I$^-$···I–C synthon acts here as a mesogenic core driving mesophase formation, which is, to some extent, independent of the alkyl chain length of the imidazolium cation. The segregation of the perfluorocarbon chains (fluorophobic effect)[15–17] promotes the self-organization of the obtained ILCs. These unconventional superfluorinated ILCs (Scheme 1) exhibit liquid crystallinity even at room temperature.[18]



Scheme 1. Chemical structures of the used imidazolium salts (**1**-*m*) and iodoperfluoroalkanes (**2**-*n*), and their halogen-bonded complexes **1**-*m*·**2**-*n*.

In the conventional design, calamitic liquid crystals normally consist of a fairly rigid core functionalized with one or more flexible alkyl or alkoxy chains.[19,20] An archetypical ILC comprises a 1-alkyl-3-methylimidazolium cation as a mesogenic core[6] and for mesophase formation to occur, the length of the alkyl chain attached to the imidazolium core is of critical importance; it has been claimed that at least a dodecyl chain is required for the system to exhibit liquid crystallinity.[21,22] Typically, lamellar mesophases are formed, driven largely by attractive, electrostatic interactions between charged species, which separate from the apolar alkyl tails.[23] However, although the imidazolium cation plays a key role in defining the mesomorphism, the counteranion is also important in influencing several physical properties of the material, phase behavior included.[6,8] For example, with the perchloroborate cluster anions $[B_{10}Cl_{10}]^{2-}$ and $[B_{12}Cl_{12}]^{2-}$, imidazolium salts with C16 and C18 alkyl chains exhibit smectic phases with very high melting and clearing temperatures,[24] whereas using the very polar fluorohydrogenate anion $[FHF]^-$,

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a smectic A phase was observed even for a C10 chain.[25] It is also generally known that while mesophases are commonly observed with, for example, small fluorinated anions such as $[BF_4]^-$ and $[PF_6]^-$, larger anions such as $[Tf_2N]^-$ do not normally support liquid-crystal phase formation. Incorporation of Eu-containing counteranions can give mesophases that show the luminescence of the anion,[26] whereas iodide appears promising when using the ILC as a hole-transporting layer in dye-sensitized solar cells.[12–14] Halide-containing anions are encountered rather frequently in ionic liquids and importantly, they can also serve as electron-donating moieties in halogen bonding.[27–29]

Halogen bonding refers to the noncovalent interaction involving a halogen atom as the electrophilic species.[30] Halogen bonding has proven to be a viable tool in crystal engineering,[31–34] and is also emerging as a noncovalent interaction of choice in designing functional supramolecular materials.[35,36] Thanks to its high directionality,[37] halogen bonding is an effective tool in constructing supramolecular liquid crystals from non-mesogenic starting compounds,[38–40] yet no halogen-bonded ILCs have been demonstrated up to date. The strength of the halogen bond can be tuned by choosing the halogen involved[41] and fluorination of the chemical groups at the vicinity of the bond-donor atoms increases the strength of resulting interactions.[42,43] The electron-donating halogen bond acceptors can be neutral Lewis bases such as pyridine groups,[44] or charged species such as mono- to tetradentate iodide anions.[27] In the latter case, the number of halogen bonds in which the anion is involved depends on both the shape and the valence of the partner.[28] Taking into account: 1) the potential of halogen bonding in constructing supramolecular liquid crystals, and 2) the ability of the commonly used halide counteranions of ionic liquids to act as halogen-bond acceptors, it seems feasible to utilize halogen bonding in designing novel types of ILCs with potentially unprecedented properties and tunability.

The complexes under investigation are derived from 1-alkyl-3-methylimidazolium iodides (**1**-*m*; where *m* is the number of carbon atoms) of varying alkyl chain length (Scheme 1). Note that only **1**-12, bearing a C12 chain, exhibits liquid crystallinity (Cr · 27 °C · SmA · 80 °C · Iso; where Cr denotes the crystal phase, SmA the smectic A phase, and Iso the isotropic liquid phase, and the values given are the phase transition temperatures),[12] whereas the others are isotropic ionic liquids. These imidazolium iodides were complexed with 1-iodoperfluorooctane (**2**-8) and 1-iodoperfluorodecane (**2**-10), which have already proven themselves as viable tectons in crystal engineering.[45]

All complexes were characterized by using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and polarized optical microscopy (POM). DSC analysis of the complex between **1**-2 and **2**-8 was consistent with the preferred 1:2 stoichiometry between the salt and the iodoperfluoroalkane. Thus, as shown in Figure 1, the DSC thermogram of the 1:3 complex shows the presence of excess pure **2**-8 (melting point 24 °C), whereas the endothermic peak at 57 °C present in the 1:1 complex corresponds to the melting of uncomplexed **1**-2. Only the thermogram of the 1:2 complex

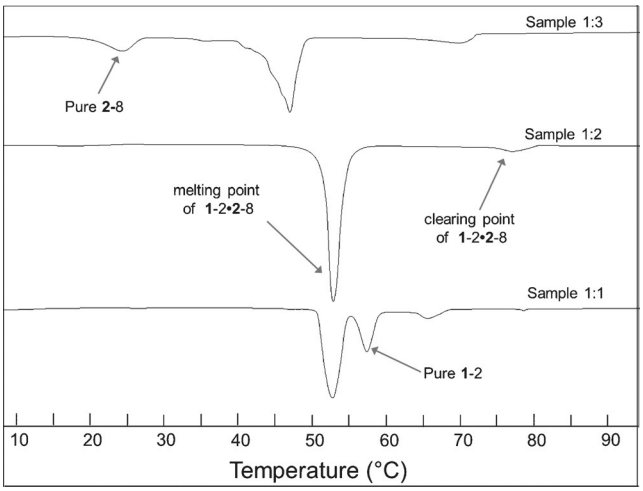

Figure 1. Thermal analysis of samples prepared by mixing **1**-2 and **2**-8 in 1:3 (top), 1:2 (middle), and 1:1 (bottom) molar ratios.

is consistent with the presence of a single species with thermal properties distinct from those of the starting compounds.

To investigate the supramolecular organization of **1**-2·**2**-8 in the solid state, single crystals were grown by slow, room-temperature evaporation of a solution of the imidazolium salt and the iodoperfluoroalkane in acetonitrile in a 1:2 molar ratio. Single-crystal X-ray analysis (see Table S1 in the Supporting Information) proved that two fluorinated chains are bound to one iodide anion; the I···I^- distances are almost identical (3.4582(9) Å and 3.4625(10) Å) and correspond approximately to 83 % of the sum of the van der Waals and Pauling radii of the iodine atom and iodide anion, respectively.[46] The C-I···I^- angles are 174.1(1)° and 175.4(2)°, consistent with the expected high directionality of halogen

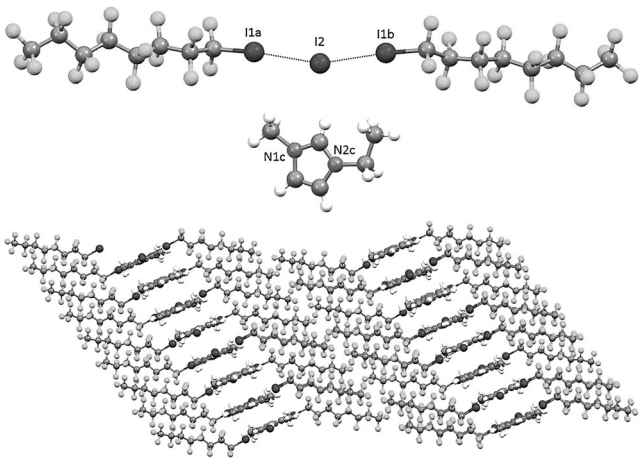

Figure 2. Halogen bonding drives the self-assembly of the imidazolium salt **1**-2 and the iodoperfluorooctane **2**-8 into the trimeric supramolecular complex **1**-2·**2**-8. Top: the asymmetric unit of the complex showing a single conformer of the disordered cation. Bottom: the packing of the structure viewed along the crystallographic *b* axis, showing the segregation between the imidazolium salt **1**-2 and the iodoperfluorooctane **2**-8. Color code: gray = carbon, nitrogen; black = iodine; light gray = fluorine; white = hydrogen. Black dotted lines indicate the halogen bonds.

bonding, and the I···I⁻···I angle is 162.38(1)° (Figure 2, top). The imidazolium cation is disordered over two equally populated conformations lying approximately on the same plane and which are related by a noncrystallographic twofold axis (as shown in Figure S1). The lower image in Figure 2 (disorder removed) shows the separation, within the crystal, between the ionic and neutral parts, as well as the segregation of perfluorocarbon chains. The structure consists of sandwich layers with cations and anions in the middle and perfluorinated chains at the external parts. These layers interact only through very weak F···F contacts, which may explain why the crystal grows as a very thin lamina (Figure 2, bottom).

The liquid-crystal (LC) properties of the halogen-bonded complex **1**-2·**2**-8 were characterized using a combination of polarized optical microscopy (POM) and DSC, with characteristic optical textures being obtained on cooling. Repeated heating and cooling cycles demonstrated that the liquid-crystalline properties are fully reversible for at least three cycles and **1**-2·**2**-8 is stable at room temperature in the open air for at least a period of one month. The complex exhibited enantiotropic LC phases and the mesomorphism was characterized as a crystal-to-SmB transition at 52.9 °C, a SmB-to-SmA transition at 68.8 °C, and a clearing point at 72.8 °C (Figure 3). The SmB phase was identified unequivocally by

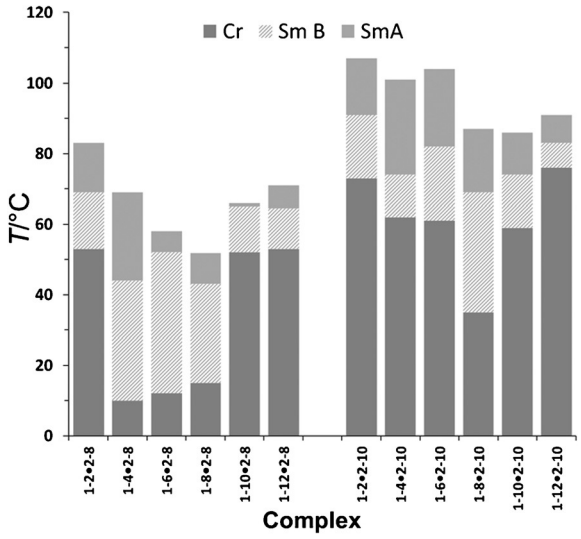

Figure 3. Thermal behavior of halogen-bonded complexes **1**-*m*·**2**-*n* as measured upon heating by hot-stage polarized optical microscopy. Gray represents the crystal phase, diagonal striations the SmB, and light gray the SmA phases.

microscopy by the appearance of characteristic striations across the back of the fans (see Figure 4, left, for SmB phase of **1**-12·**2**-10 complex), which disappeared on cooling further below the transition. Moreover, the fact that homeotropic areas of the SmA phase remained homeotropic through the transition along with the fluidity of the mesophase suggests the occurrence of the only other possible uniaxial liquid-crystalline mesophase in calamitic systems, that is, the SmB phase.

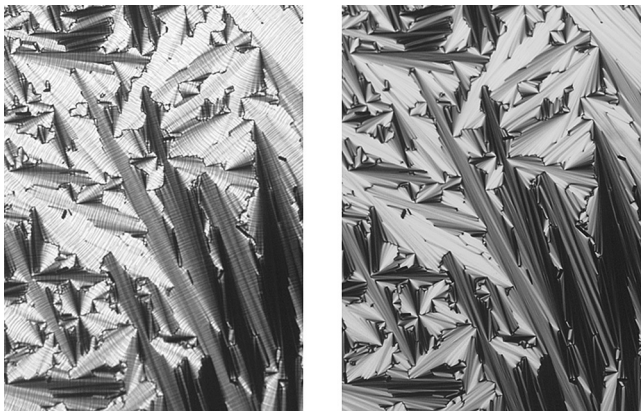

Figure 4. Optical textures of the smectic phases observed for **1**-12·**2**-10 on cooling from the isotropic state. Left: SmB phase at 77 °C; Right: SmA phase at 83 °C (crossed polarizers).

Taking into account these data, we synthesized all of the complexes presented in Scheme 1 using a 1:2 molar ratio between the imidazolium salts and the iodoperfluoroalkanes. As exemplified in DSC/TGA analyses on the sample containing the imidazolium salt **1**-12 and the iodoperfluoroalkane **2**-10 in 1:2 ratio, a single solid species is obtained, which releases quantitatively the iodoperfluorodecane in a temperature range much higher than the unbound compound (Figures S2, S3).

POM studies revealed that all **1**-*m*·**2**-*n* complexes were liquid crystalline, some even at room temperature, with SmB and SmA phases (Figures 3, Figure 4). Table S2 reports the phase-transition temperatures for all of the complexes presented in Scheme 1.

Given that 1-alkyl-3-methylimidazolium cations with alkyl chains as short as ethyl are not known to induce liquid crystallinity, the remarkable thing about these new materials is that the mesomorphism is enabled by the rigid rod-like structure of the halogen-bonded supramolecular anion. With the exception of simple salts of carboxylic acids,[41] such an observation is, at best, rare. Thus, the mesomorphism evidently arises as the anion is highly anisotropic owing to the fact that iodoperfluoroalkanes are very much "stiffer" than analogous hydrocarbon chains, being locked in a distorted *trans* arrangement by the repulsion between 1,3-disposed CF_2 groups.[42,43] Moreover, two such chains adopt, in the complexes, an effectively linear arrangement about the central iodide anion. This is then consistent with the observation that the transition temperatures for complexes with the anion prepared from iodoperfluorodecane (**2**-10) are generally higher than those with anion from **2**-8, as the former is a longer rod. Furthermore, the observation of SmB and SmA phases is consistent with the known tendency[44,45] of perfluoroalkyl chains to give rise to lamellar mesophases, a manifestation of nanophase segregation. These phases are also those most commonly seen in ILCs.[5]

Crystallization was ineffective in affording all of the complexes reported in Scheme 1 apart from **1**-2·**2**-8; the complexes were thus prepared from the melt.[47] A small amount of biphasic behavior at melting and clearing points was detected, indicative of slightly incomplete complex

formation. However, the efficacy and reliability of the melt methodology was confirmed by the observation that the phase behavior of **1**-2·**2**-8 prepared through crystallization and in the melt was the same.

The melt method was carried out in a sealed system in order to avoid issues with the volatility of the iodoperfluoroalkanes. The materials clearly have the correct overall composition but with two halogen bonds to form, there is a chance that the supramolecular integrity is not perfect. This would account for the slightly uneven pattern in the thermal behavior of some of the complexes of **2**-10.

The mesophase behavior of complexes **1**-*m*·**2**-8 shows a monotonic decrease in clearing points as the chain length in **1**-*m* increases from $m=2$ to $m=8$. The next homologue, **1**-10·**2**-8, shows a much enhanced melting point compared to **1**-8·**2**-8 and greater stability for both the SmA and SmB phases. The behavior of **1**-12·**2**-8 is similar. An analogous pattern of monotonic decrease in clearing point is also found for complexes **1**-*m*·**2**-10, with a minimum in the crystal phase stability for cation **1**-8 that recovers with longer cation chain length. The observation that the clearing points for the materials afforded by **2**-10 (longer and, therefore, more anisotropic) are higher than those afforded by **2**-8 is totally consistent with the proposition that the mesomorphic behavior is enabled by the supramolecular rod-like anion.

To summarize, we report on unconventional ionic liquid crystals in which the liquid crystallinity is enabled by halogen-bonded supramolecular anions $[C_nF_{2n+1}\text{-}I\cdots I\cdots I\text{-}C_nF_{2n+1}]^-$ that act as rigid rod-like calamitic units. The material system is unique in many ways, demonstrating for the first time 1) ionic, halogen-bonded liquid crystals, and 2) imidazolium-based ionic liquid crystals in which the liquid crystallinity is not driven by the alkyl chains of the cation. Indeed, with our supramolecular design, even salts of the 1-ethyl-3-methylimidazolium cation exhibit smectic mesophases. It is also important that some of the complexes reported herein are mesomorphic even at room temperature. The superfluorinated ionic liquid crystals reported in this Communication may pave the way towards totally new design principles in liquid-crystalline materials and develop as an attractive platform for new functional materials.

Experimental Section

Single crystals of **1**-2·**2**-8 were prepared by dissolving, separately, 1-methyl-3-ethylimidazolium iodide and 1-iodoperfluorooctane in acetonitrile at room temperature in a 1:2 molar ratio, under saturated conditions. The two saturated solutions were then mixed in a clear borosilicate glass vial, which was left open in a closed cylindrical wide-mouth bottle containing paraffin oil. The solvent was allowed to slowly evaporate at room temperature until yellow crystals, suitable for X-ray analysis, were formed. Both the crystallization and melt methods (see the Supporting Information) afforded the same complexes as confirmed by DSC and POM analyses.

Single-crystal XRD data for **1**-2·**2**-8: $C_{22}H_{11}F_{34}I_3N_2$, $M_r=1329.995$, triclinic, $P\text{-}1$, $a=7.662(2)$ Å, $b=9.723(2)$ Å, $c=26.220(6)$ Å, $\alpha=99.83°$, $\beta=91.33(2)°$, $\gamma=91.03(2)°$, $V=1923.65$ Å^3, $T=220(2)$ K, $Z=2$, 41341 reflections measured, 11564 independent reflections, 622 parameters, 235 restraints, $\theta_{max}=30.57°$, $R[F^2>2\sigma(F^2)]=0.0414$ $wR(F^2)=0.0910$. CCDC 1446403 (**1**-2·**2**-8) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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